Acid-Base Equilibria in Dioxane-Water Mixtures
of Low Water Content

JOUKO KOSKIKALLIO and ANJA ERVASTI

Department of Chemistry, University of Oulu, Oulu, Finland

The apparent equilibrium constants of the proton exchange be-
tween o-chloroaniline and perchloric, hydrochloric and sulphuric
acid in dioxane-water mixtures have been measured spectrophoto-
metrically. The results agree qualitatively with the conclusions drawn
from previous kinetic experiments [2,3] that the apparent acid strength
of perchloric acid increases greatly, that of sulphuric acid increases
slightly, and that of hydrochloric acid decreases as the amount of
water in dioxane decreases in dioxane rich solvent mixtures.

Values of the acidity function H_0 in dioxane-water and acetone-water mixtures
were measured by Braude and Stern [1], who used fairly concentrated, 1 M
and 0.1 M, hydrochloric acid solutions. Recent kinetic studies [2,3] of some acid-
catalysed hydrolysis reactions have shown that the apparent acid strengths of
strong mineral acids differ greatly in dioxane-water mixtures of low water
content. This study was undertaken in order to obtain values of the equilibrium
constants for some acid-base reaction which could be compared with the kinetic
results. o-Chloroaniline was chosen as the base because its basicity is suitable
for measurements in solvent mixtures containing mineral acids in concentra-
tions varying from about 10^{-1} to 10^{-3} M.

EXPERIMENTAL

Materials. All the chemicals used (E. Merck AG, *pro analysi*) were used as such except
dioxane (Fluka AG, purified by the method of Hess and Frahm) from which traces of
hydroxylic compounds were removed by repeated treatment by the method of Hess and
Frahm [4]. Hydrogen chloride prepared from sodium chloride and 95 % sulphuric acid was
dissolved in dioxane. The solutions containing perchloric acid were prepared from aqueous
70 % perchloric acid. Freshly distilled water was used in all experiments.

Method. A Beckman DU spectrophotometer was used to measure the extinctions of
the solutions. The concentration of o-chloroaniline was the same, about 10^{-4} M, in all expe-
riments. Absorptions at several wavelengths around that where the absorption was
maximal were measured. The extinction E_∞ of the o-chloroanilinium ion (or ion pair)
was obtained by measuring the absorbtion of solutions containing mineral acid in great
excess or by substituting two extinction values obtained at low acid concentrations in
eqn. (2).

Table 1. Spectrophotometrically measured values of the equilibrium constant K = [HA][I]/[IH$^+$] in dioxane-water mixtures at 20°C. I = *o*-chloroaniline, HA = HClO$_4$, HCl or H$_2$SO$_4$.

[H$_2$O] mole/l	Acid	10^4 × [Acid] mole/l	K × 10^4 mole/l
0.108	HClO$_4$	4.84	0.61
0.108		3.73	0.63
0.22		3.76	2.24
0.45		4.84	7.93
0.45		3.76	8.10
0.45		46.4	6.87
1.11		35.8	63.1
2.22		386	184
2.22		468	173
4.34		364	565
6.56		470	615
8.82		364	851
11.1		364	773
0	HCl	480	451
0		544	582
0.026		840	380
0.069		210	472
0.069		388	300
0.069		908	258
0.278		210	280
1.11		183	129
2.22		207	207
5.48		814	660
11.1		832	1 005
0.11	H$_2$SO$_4$	199	86
0.232		262	99
0.55		248	148
0.99		454	193

The ratio of the concentrations of *o*-chloroaniline (I) and *o*-chloroanilinium ion (IH$^+$) were obtained by substituting the experimental extinction values in eqn. (1) and they were used to calculate the equilibrium constant K, eqn. (2).

$$\frac{[I]}{[IH^+]} = \frac{E_0 - E}{E - E_\infty} \tag{1}$$

E_0 is the extinction of the solution of *o*-chloroaniline and E the extinction of the solution containing *o*-chloroaniline and mineral acid. In dioxane-rich dioxane-water mixtures ions such as the *o*-chloroanilinium ion IH$^+$ and hydrogen ion H$^+$ are present mainly as ion pairs which complicates the interpretation of the experimental data [5,6]. The apparent equilibrium constant K was calculated from the experimental data.

$$K = \frac{[HA][I]}{[IH^+]} = [HA]\frac{E_0 - E}{E - E_\infty} \tag{2}$$

[HA] is the analytical concentration of the mineral acid.

DISCUSSION

Three different acid concentrations in the ratios 1:2:3 were used in the experiments. The calculated values of K were constant within the chosen concentration ranges when perchloric or sulphuric acid was used but decreased when
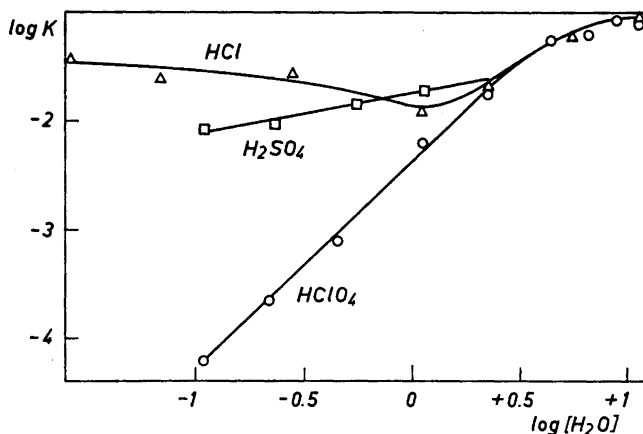
Fig. 1.

the acid concentration increased in the case of hydrochloric acid. The mean values of K obtained at different acid concentrations are given in Table 1 together with the mean values of the acid concentrations. These values show that a tenfold increase in the concentration of perchloric acid has a very small effect on the value of K, but a similar change in the concentration of hydrochloric acid affects the equilibrium constant considerably. This difference may be due to the much higher concentrations of hydrochloric acid used.

In the presence of perchloric acid, a rapid decrease occurs in the value of K when the content of water in dioxane is decreased. The plot (Fig. 1) of log K *versus* log $[H_2O]$ is an approximately straight line with a slope of about 1.9. The apparent acid strength of perchloric acid in dioxane containing 0.1 mole of water per litre is about a thousand times as great as its strength in dioxane containing 10 moles of water per litre. The value 1.9 of the slope indicates that two water molecules are liberated when the proton is transferred to the chloroaniline molecule in reaction 3. The proton is therefore solvated by at least two water molecules in the solvent mixtures studied. It is very likely that the proton is solvated by approximately four water molecules in water and water-rich solutions [7] and by two water molecules in acetic acid-water mixtures containing about 1 to 10 moles of water in acetic acid [5,8] but by only one water molecule in acetic acid containing water less than 0.4 moles per litre [5]. Also in methanol-water and ethanol-water mixtures the proton is solvated by only one water molecule [9].

The hydrolysis rates of diethoxymethane [2] and acetic anhydride [3] in the presence of perchloric acid as catalyst in dioxane-water mixtures increase rapidly when the amount of water decreases from about 10 moles per litre. This also indicates that perchloric acid is a much stronger acid in solvent mixtures containing low concentrations of water. The plots of log k *versus* log $[H_2O]$ are straight lines with slopes of -2.5 and -1.7, respectively. The opposite signs of the slopes derived from kinetic and equilibrium measurements are due

to the way in which K is defined (eqn. 2). In spite of the different nature of the bases in the two cases, the proton being attached to an oxygen atom in case of diethoxymethane and acetic anhydride and to a nitrogen atom in case of o-chloroaniline, and the ion pair formation the slopes have similar values. The experiments could not be extended to dry dioxane because of the oxidating power of perchloric acid.

When hydrochloric acid was used the value of K changed in the opposite direction when the solvent composition was altered indicating that hydrochloric acid is a weaker acid than perchloric acid in solvent mixtures containing small amounts of water. The slope of the straight part of the curve in Fig. 1 is about -0.2. In water-dioxane mixtures containing about 2 to 10 moles of water per litre, the values obtained with hydrochloric acid and perchloric acid are practically identical. It seems therefore probable that hydrochloric acid dissolved in dioxane-water looses its solvation water when the concentration of water in the solvent mixtures decreases below about 2 moles per litre.

The kinetic experiments [2,3] revealed somewhat larger effects when hydrochloric acid was used. The rates of the acid-catalysed hydrolyses of diethoxymethane and acetic anhydride decreased when the amount of water in dioxane decreased below about 2 moles per litre. The slopes of the plots of log K versus log $[H_2O]$ were 1.5 and 1.6, respectively.

A change in the composition of dioxane-water mixtures altered the equilibrium constant K to only a small extent when sulphuric acid was the acid. The slope of the curve in Fig. 1 is 0.4 and thus close to the values -0.5 and 0.1 obtained in the kinetic experiments [2,3]. The apparent acid strength of sulphuric acid remains almost unaltered in the range of the dioxane-water mixtures used in the present experiments. The apparent acid strength of the mineral acids studied decrease in the order $HClO_4 > H_2SO_4 > HCl$ in dioxane rich solvent mixtures. In acetic acid the pK values and the apparent acid strengts decrease in the same order [5].

REFERENCES

1. Braude, E. A. and Stern, E. S. *J. Chem. Soc.* **1948** 1976.
2. Koskikallio, J. and Tarvainen, I. *Acta Chem. Scand.* **16** (1922) 263.
3. Koskikallio, J. and Ervasti, A. *Suomen Kemistilehti* **B34** (1961) 111.
4. Hess, K. and Frahm, H. *Ber.* **71** (1938) 2627.
5. Bruckenstein, S. *J. Am. Chem. Soc.* **82** (1960) 307.
6. Hummelstedt, L. E. and Hume, D. N. *J. Am. Chem. Soc.* **83** (1961) 1564.
7. Bascombe, K. N. and Bell, R. P. *Discussions Faraday Soc.* **24** (1957) 158.
8. Wiberg, K. B. and Evans, R. J. *J. Am. Chem. Soc.* **80** (1958) 3019.
9. Koskikallio, J. *Acta Chem. Scand.* **13** (1959) 671.